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Title: The Use of Sodium Dithionite for the Remediation of Hexavalent Chromium in Mortendad Canyon

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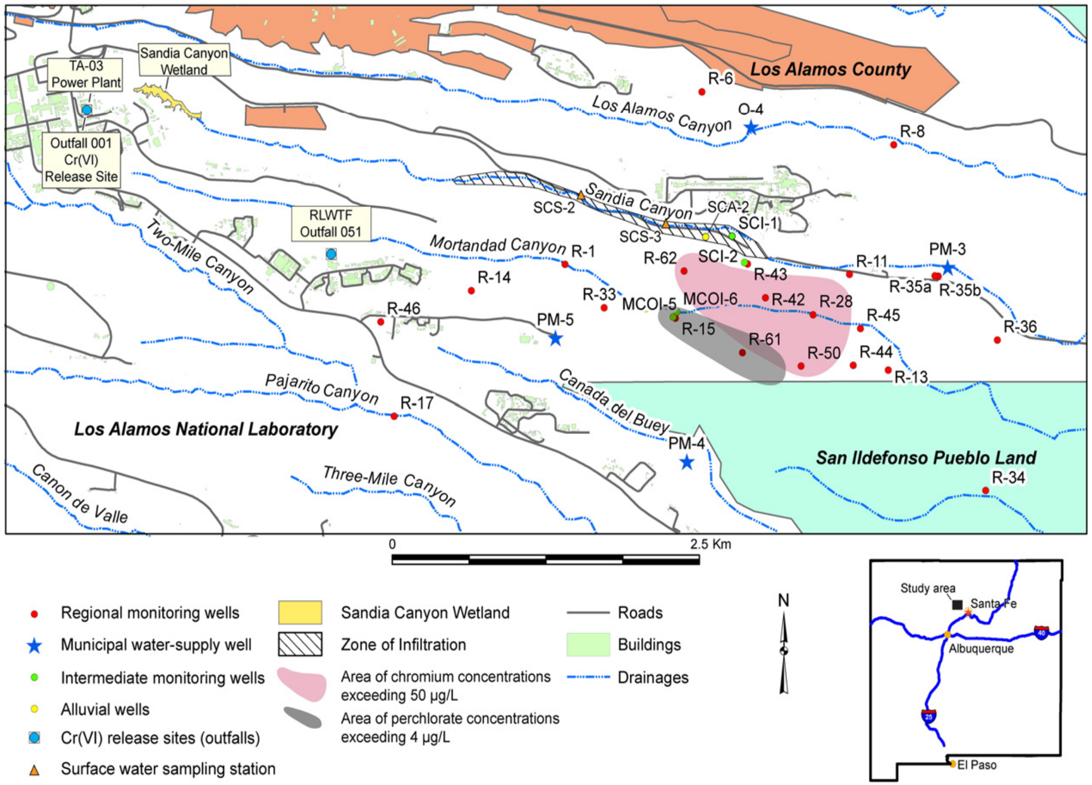
The Use of Sodium Dithionite for the Remediation of Hexavalent Chromium in Mortandad Canyon

Katherine TelfeyanEarth System Observations EES-14 Radiogeochemistry Group

February 15, 2017

Cr(VI) Plume in Groundwater at LANL



Heikoop et al., 2014

- Cr(VI) highly soluble and toxic
- Used as anti-corrosion agent in mid 1900s
- Effluent has led to legacy waste
- Remediation requires use of in-situ redox barrier

Sodium Dithionite ($Na_2S_2O_4$)

- **Strong reducing agent**
- **Industrial uses and environmental remediation**
  - $S_2O_4^{2-} + 2Fe(III)_{(s)} + 2H_2O = SO_3^{2-} + 2Fe(II)_{(s)} + 4H^+$
  - $3Fe(II)_{(s)} + HCrO_4^- + 4H^+ = Cr(OH)_{3(s)} + 3\ Fe(III)_{(s)} + 2H_2O$
- **Degrades rapidly in the presence of oxygen or in water**
  - Previously reported reaction products: SO_3^{2-}, $S_2O_3^{2-}$, H^+
- **No uniform degradation rate and reaction mechanism**
  - Slower degradation in alkaline solution
  - Longest record of dithionite in solution: 2-3 weeks

Study Objectives

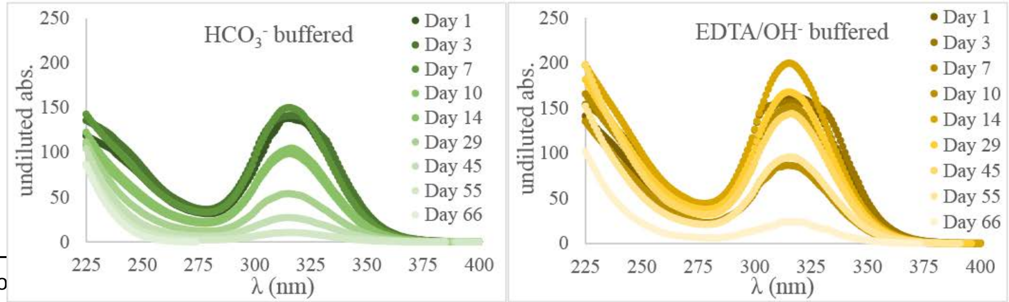
I. **Determine the degradation rate and products of dithionite in anaerobic alkaline aqueous solution**

II. **Determine the reduction capacity of dithionite-treated sediments for Cr(VI)**

I. Dithionite Decomposition in Aqueous Solution Methods

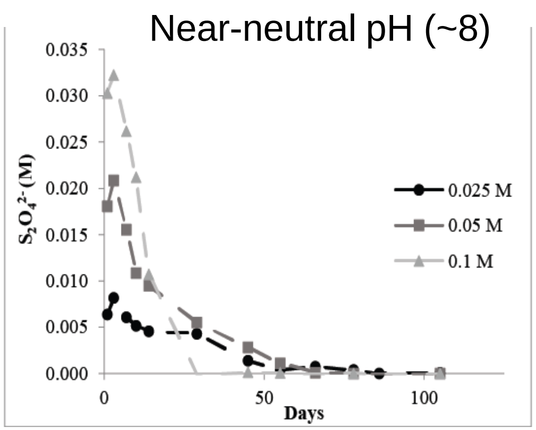
- **Dithionite solutions of varying concentrations (0.1 M, 0.05 M, 0.025 M) prepared in unbuffered solutions, 0.1 M bicarbonate solution (pH ~8), Fisher buffer solution of EDTA/carbonate/tetraborate/hydroxide (pH~10)**
- **Immediately flame sealed to prevent oxygen intrusion or loss of H_2S**
- **Measurements taken over 100 days**
  - Ion Chromatography: Oxidized S (SO_4^{2-})
  - Iodometric Titration: Total Reduced Sulfur (Σ $S_2O_4^{2-}$, SO_3^{2-}, $S_2O_3^{2-}$, H_2S/HS^-, polythionates (except $S_2O_6^{2-}$)
    - UV-vis analysis: $S_2O_4^{2-}$ and SO_3^{2-}
    - Titration with formaldehyde: $S_2O_3^{2-}$
    - Precipitation with $Cd(CH_3COO)_2$ and titration with iodine: H_2S/HS-
  - Missing: S as zero-valent S or in polysulfane chains

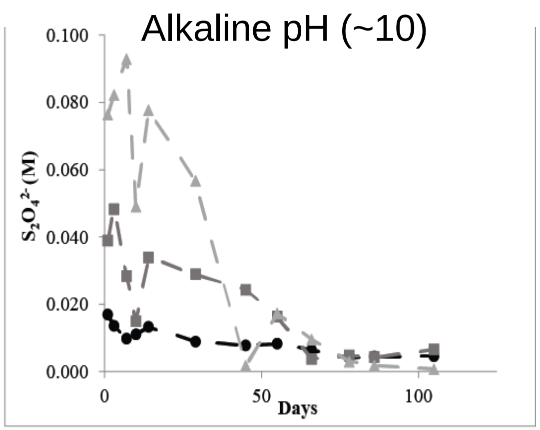
Dithionite ($S_2O_4^{2-}$) Degradation Through Time Monitored by UV-vis

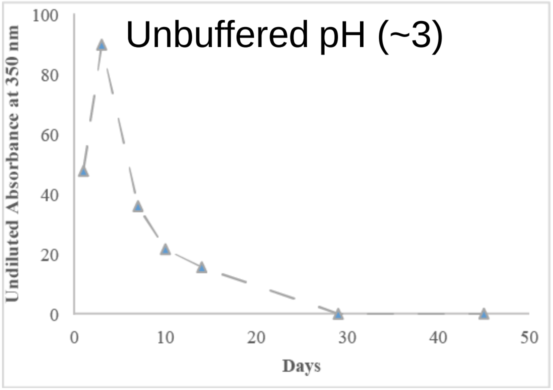


I. Dithionite Decomposition in Aqueous Solution
Results-Dithionite

- **Loss of dithionite more rapid at low pH**
- **0.05 M and 0.025 M solutions of unbuffered dithionite completely hydrolyzed in <1 day**
- **Half-life dithionite in near-neutral buffer: 10.7 days**
- **Half-life in alkaline buffer: 33.6 days**
- **Dithionite measureable at highest pH for 105 days and at near-neutral pH for 50-60 days**

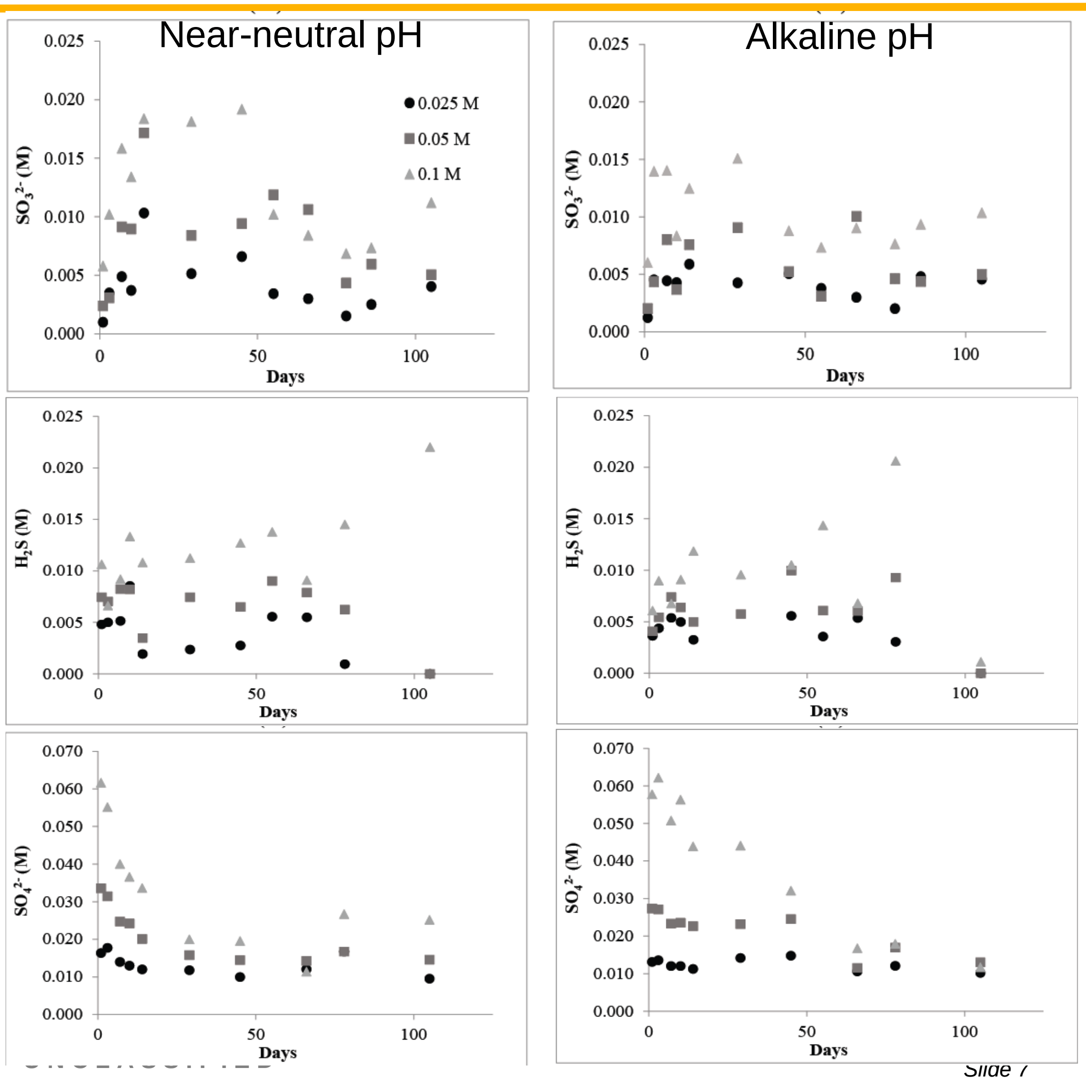






I. Dithionite Decomposition in Aqueous Solution
Results-Degradation Products

- **No $S_2O_3^{2-}$ present**
- **H_2S/HS^-, SO_3^{2-}, SO_4^{2-} significant products**
- **Sulfur mass balance yields "missing reduced S" not determined by current methods**
  - Accounts for ~10 % in alkaline pH solution, ~30 % in near-neutral of total S
  - Possibly zero valent sulfur, some of the polythionates, elemental sulfur
  - $S_4O_6^{2-}$



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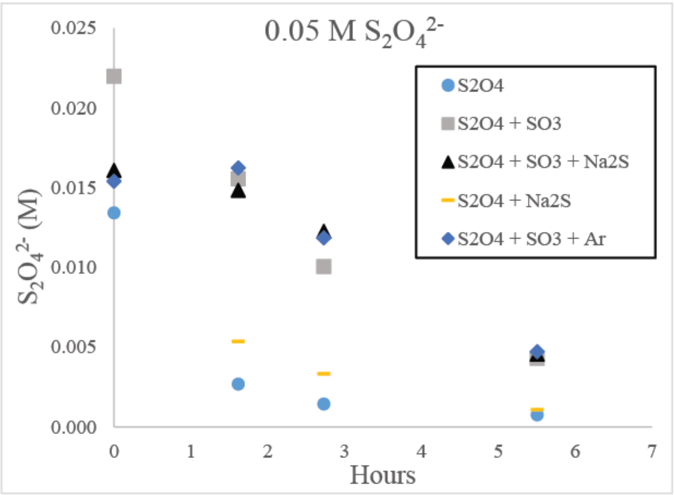
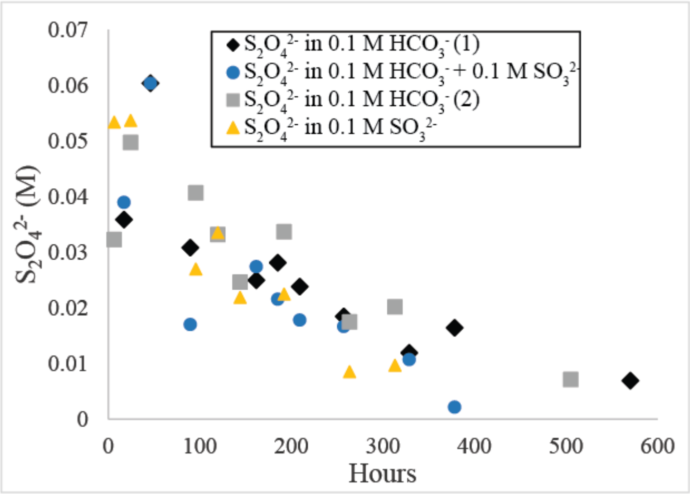
I. Dithionite Decomposition in Aqueous Solution Results-Hydrolysis Reaction and Kinetic Law

- **Stoichiometry determined from reaction products**
- **Near-neutral pH, represents relatively rapid degradation**
  - $4\ S_2O_4^{2-} + H_2O = HS^{-} + SO_3^{2-} + 2\ SO_4^{2-} + S_4O_6^{2-} + H^{+}$
- **At more alkaline pH and over longer time scales:**
  - $3\ S_2O_4^{2-} + 3\ H_2O = 2HS^{-} + SO_3^{2-} + 3\ SO_4^{2-} + 4\ H^{+}$

- **Rate-law determined to be first order with respect to dithionite and fractional order with respect to [H+]**
  - $\frac{dC_i}{dt} = S_i 10^{-4.81}\{H^+\}^{0.24}\{S_2O_4{}^{2-}\}$ (Si: stoichiometric coefficient of i, Ci: concentration of i)
  - Decomposition a function of pH not previously incorporated into rate laws

Buffer Solutions





- **Aquifers near saturation with respect to calcite**
  - Buffer the solution during field injection while maintaining circumneutral pH using reaction products of dithionite degradation

II. Batch and Column Experiments Methods

- **Sediments from Mortendad Canyon treated with $Na_2S_2O_4$ in batch and column experiments**
  - Determine reduction capacity of sediment with optimal $S_2O_4^{2-}$ concentration
  - Determine potential release of harmful byproducts (As, Mn, SO_4^{2-})

- **Batch Experiments**
  - 5g 4 different sediments treated with 0.025 M, 0.05 M, 0.1 M dithionite buffered with HCO_3^-
  - Sampled over 43 days for $S_2O_4^{2-}$, SO_4^{2-}, pH, trace metals (Fe, Mn, Cr, As)
  - Added excess Cr(VI) solution to treated sediments to determine maximum reduction capacity

II. Batch and Column Experiments Methods

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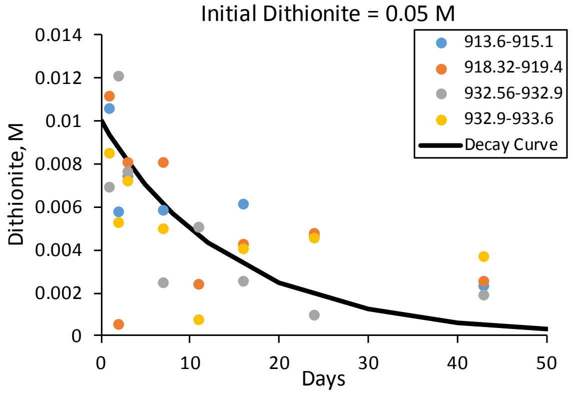
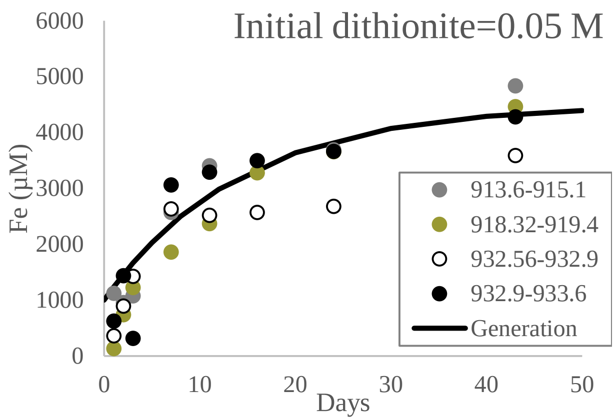
  - Determine reduction capacity of sediment with optimal $S_2O_4^{2-}$ concentration
  - Determine potential release of harmful byproducts (As, Mn, SO_4^{2-})
- **Column Experiments**
  - 230 g sediment in columns with 60 mL pore volumes, residence time 2 days
  - 2 pore volumes of 0.05 M $Na_2S_2O_4$ buffered with 0.05 M Na_2SO_3 and 400 ppm LiBr tracer in background solution of Cr(VI) contaminated water from Mortendad Canyon (900 ppb) followed by injection of contaminated aquifer water until breakthrough of Cr(VI)
  - Eluent measured for major ions, major cations, trace metals
  - Treated sediment cut into 1 cm intervals and leached with 2 M HNO_3

II. Batch and Column Experiments
Batch Results

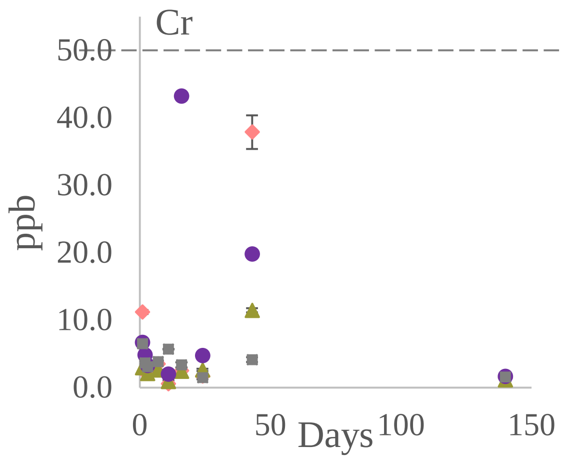
- **Loss of dithionite by 43 days & production of Fe**
  - Rapid decomposition of dithionite: $4\ S_2O_4^{2-} + H_2O = HS^- + SO_3^{2-} + 2\ SO_4^{2-} + S_4O_6^{2-} + H^+$
  - 0.01 M extra $S_2O_4^{2-}$ lost compared to blank experiments: $S_2O_4^{2-} + 2Fe(III)(s) + 2H_2O = SO_3^{2-} + 2Fe(II)_{(s)} + 4H^+$
  - Per g of sediment: consume $2x10^{-5}$ moles $S_2O_4^{2-}$ and generates $2x10^{-6}$ moles Fe
  - First-order decomposition rate after initial decomposition and assume that 0.35 moles of Fe generated for every mole of dithionite consumed
  - After 150 days Fe(II) readsorbs/reprecipitates

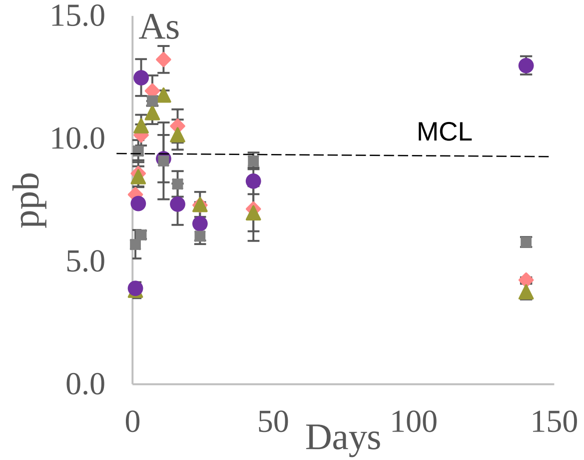




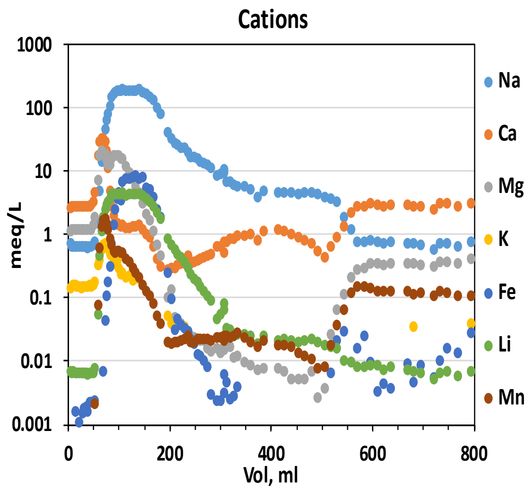
II. Batch and Column Experiments
Batch Results

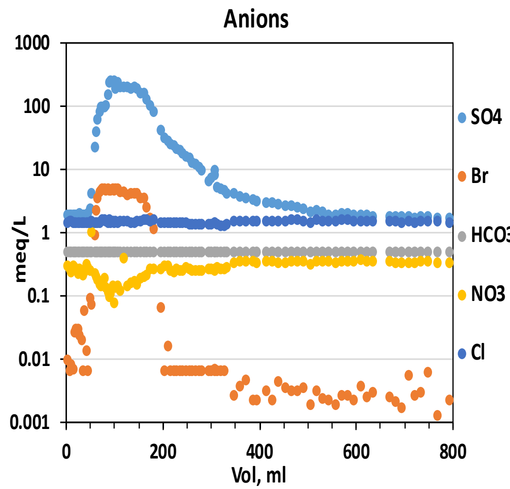
- Cr and As near to below MCL
- Max Cr uptake from treated sediments 1500-2500 mg Cr/kg sediment
- 30-99% of all Fe in the sediments required for this reduction
- No correlation between uptake and Fe or surface area
- Fe cannot account for all of the reductive capacity generated by the sediments

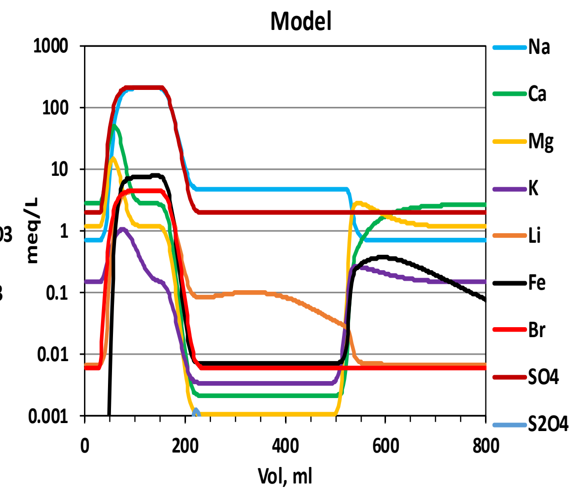




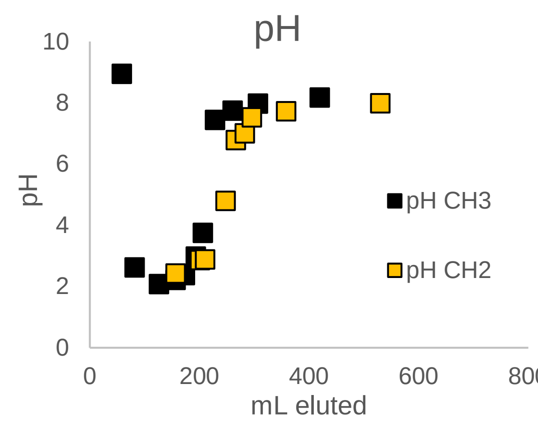
II. Batch and Column Experiments
Column Results



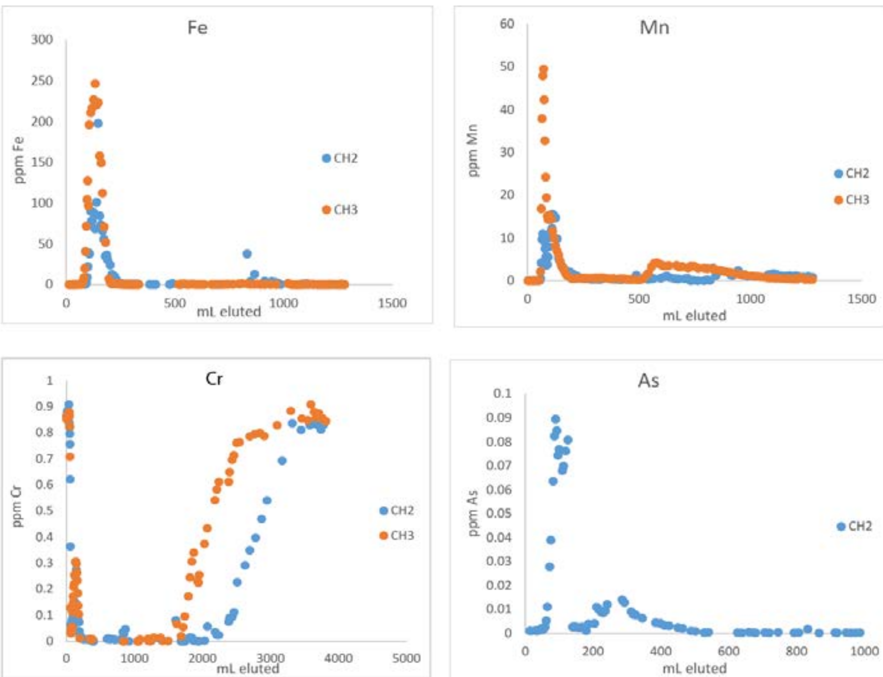


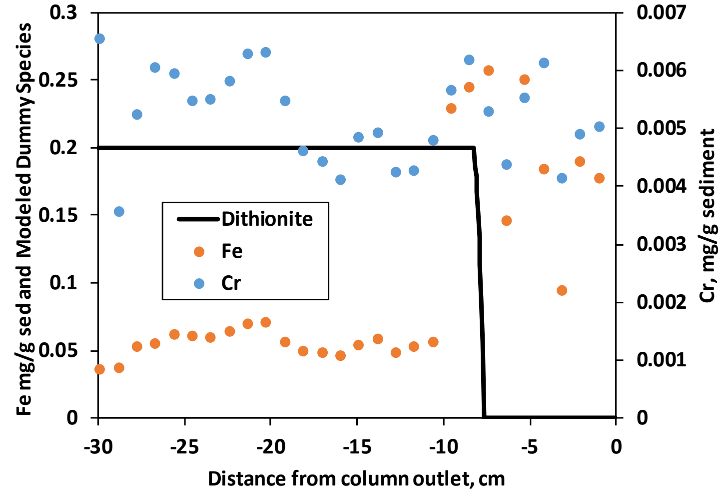


- Cation exchange reactions during injection of Li and Na
- pH drops to ~ 3. 4 moles of H+ are produced for every 2 moles of Fe(III) reduced



II. Batch and Column Experiments
Column Results





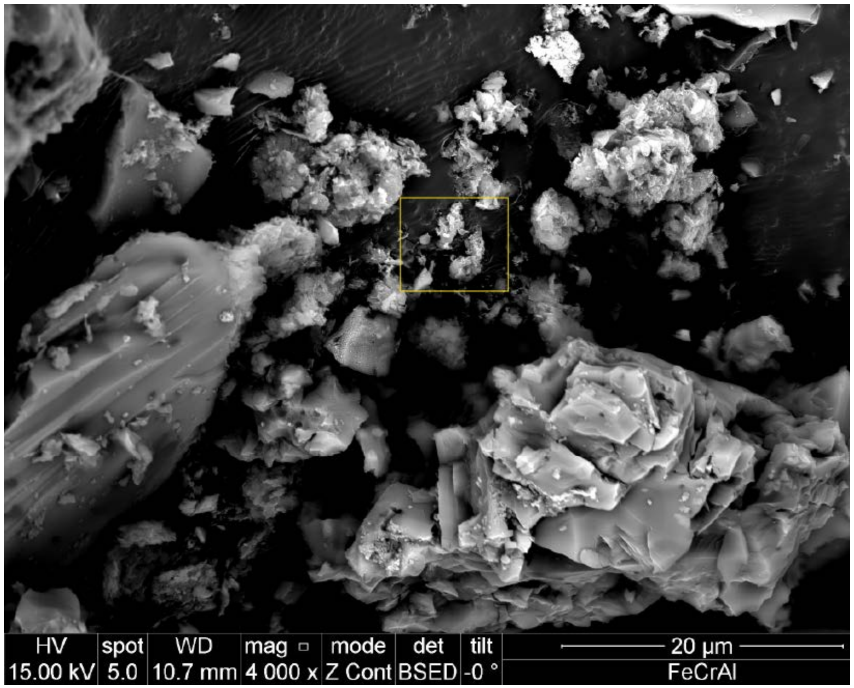
- Release of Fe, Mn, Cr, and As during dithionite injection and subsequent decline
- Cr breakthrough occurs after ~ 30-50 pore volumes
- Puye (CH2) greater reduction capacity – more Fe retained in the column (crystalline phases)

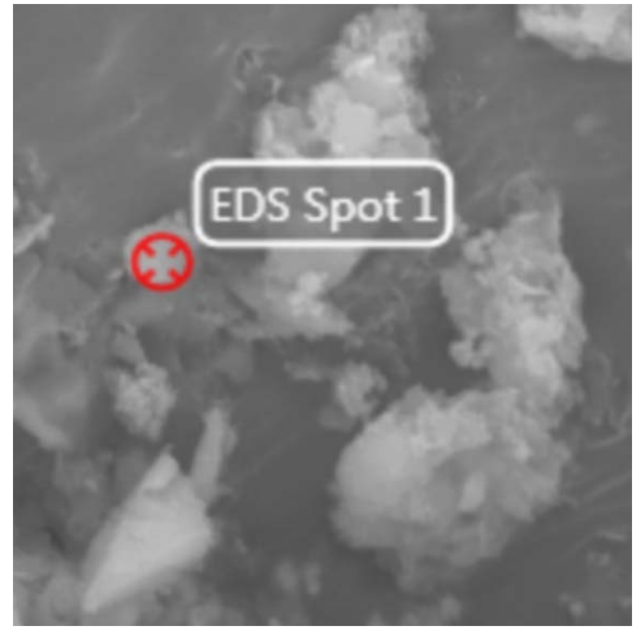
- Sediment leached with 2% HNO_3
- Predict dithionite dissolution of Fe occurred through 2/3 of the column and redeposited by cation exchange
- Cr reduction and precipitation independent of Fe

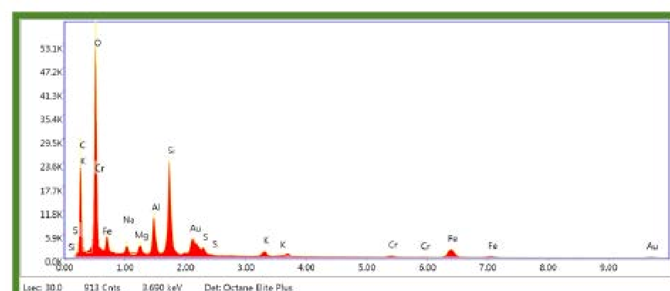
II. Batch and Column Experiments
Sulfur

- **Mass balance of S into and out of columns suggests loss of S to column….FeS minerals?**
- **Addition of Cr(VI) to treated sediments in batch experiments suggest >100% efficiency in reduction if only Fe(II) is being oxidized.**
- **Is S from the dithionite injection reacting with the sediment and contributing to its reduction capacity?**
- **Current and Future Work**
  - Determine S speciation in sediment and effect on Cr(VI) reduction
  - Ongoing field pilot tests

SEM


HV
15.00 kV
spot
5.0
WD
10.7 mm
mag
4 000 x
mode
Z Cont
det
BSED
tilt
-0 °
20 µm
FeCrAl


EDS Spot 1


53.1K
47.2K
41.3K
35.4K
29.5K
23.6K
17.7K
11.8K
5.9K
0.0K
O
C
Cr
Si
Al
Na
Mg
Fe
Au
S
K
0.00
1.00
2.00
3.00
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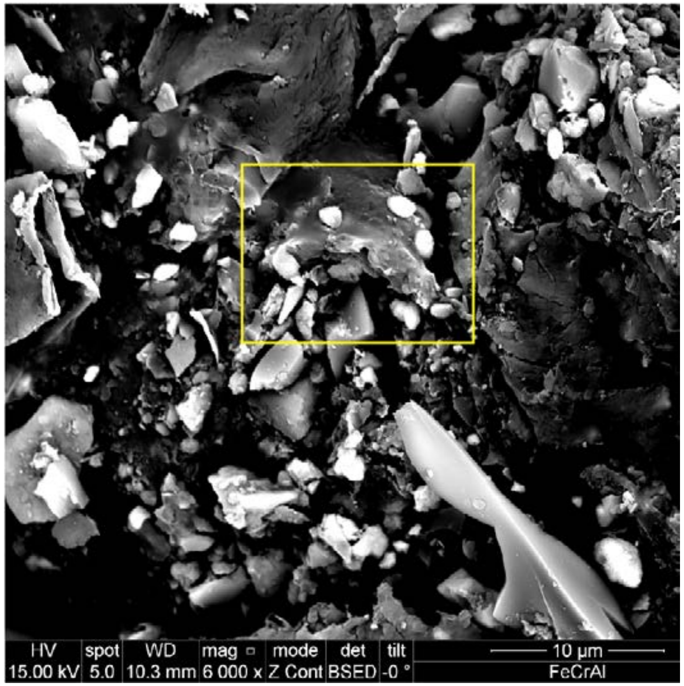
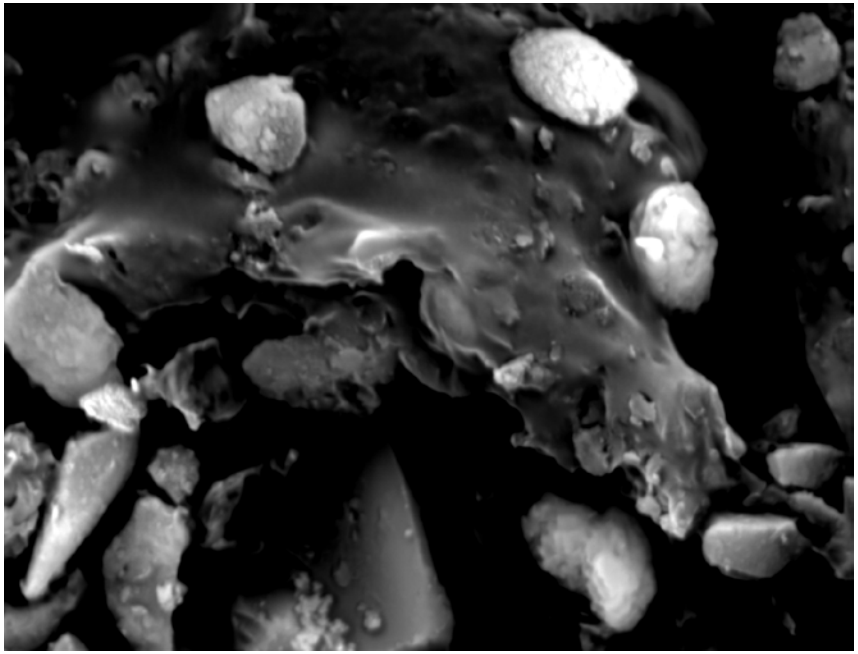
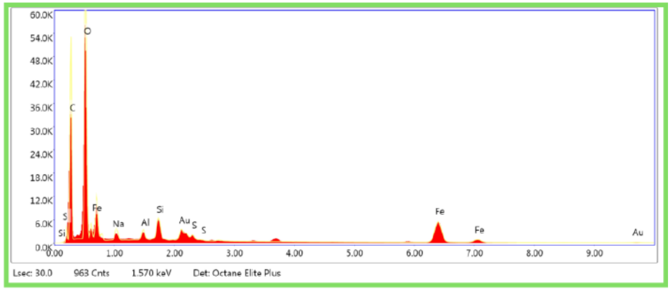
7.00
8.00
9.00
Lsec: 30.0
913 Cnts
3.690 keV
Det: Octane Elite Plus

SEM



HV 15.00 kV
spot 5.0
WD 10.3 mm
mag 6 000 x
mode Z Cont
det BSED
tilt -0 °
10 µm
FeCrAl





O
C
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60.0K
54.0K
48.0K
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36.0K
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18.0K
12.0K
6.0K
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0.00 1.00 2.00 3.00 4.00 5.00 6.00 7.00 8.00 9.00
Lsec: 30.0 963 Cnts 1.570 keV Det: Octane Elite Plus

Dithionite Study Conclusions

- **Blank experiments demonstrate that $S_2O_4^{2-}$ exists in a closed system, such as a confined aquifer, for longer than previously expected**
  - H_2S/HS^- is an important reaction product previously overlooked. Failure to thoroughly maintain a closed system may have led to shorter predicted dithionite lifetimes in previous studies
- **$S_2O_4^{2-}$ effectively reduces sediment $Fe(III)_{(s)}$ to $Fe(II)_{(s)}$, releasing minor amounts of $Fe(II)_{(aq)}$**
- **Mn and As release during dithionite injection likely linked with Fe release during reduction and ion exchange. After injection, concentrations return to background.**
- **With extended contact time (batch experiments), dithionite-treated sediments may remove up to 2500 mg Cr/kg sediment. Column studies suggest that dithionite-treated sediments will remove up to 30 pore volumes of contaminated water (900 ppb Cr(VI)).**
- **Fe is not exclusively responsible for the reduction capacity imparted to the sediments from the dithionite treatment.**

Thank you!!

- Thanks to Rose Harris, Doug Ware, and Sarah Sams for assistance with sampling
- Kai Williams, David Chu, and Oana Marina for ICP and IC analysis
- Sachin Pandey and Velimir Vesselinov for kinetic modeling
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